# Pd-Cu Alloy Composite Membranes for High Temperature Hydrogen Separation

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# Outline

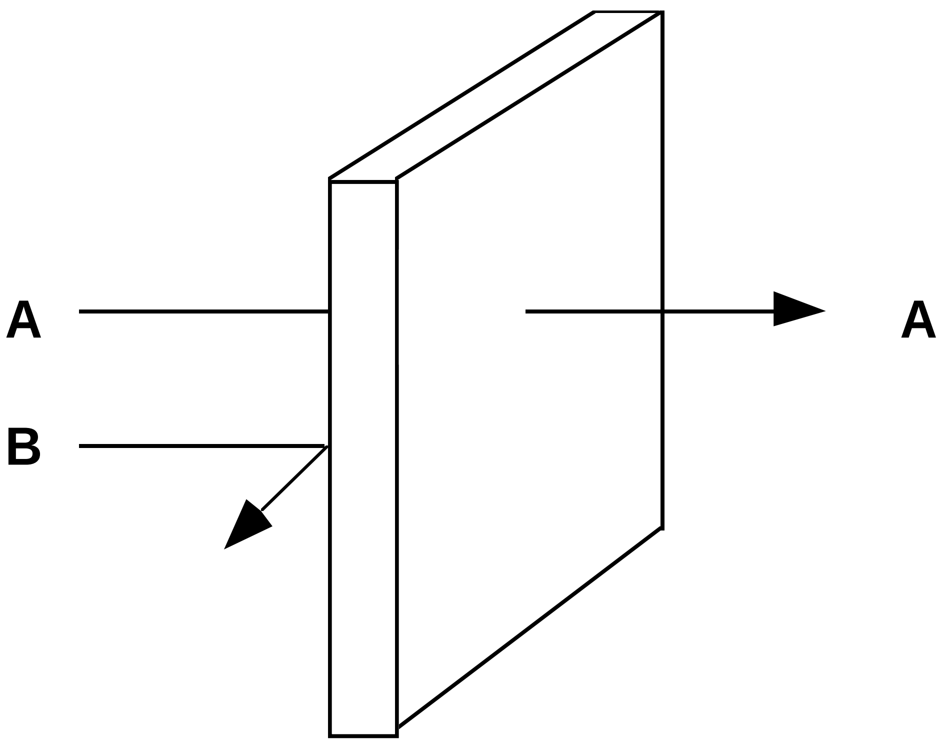
- Project objectives
- Why Pd membranes?
- Why Pd alloys?
- Fabrication by electroless plating
- DOE pure $H_2$ flux targets
- Flux of thin Pd-Cu composite membranes
- Effect of gas mixtures
- Inhibition of $H_2$ flux due to CO, $CO_2$, $H_2O$, and $H_2S$
- Future Work and Conclusions

# Project Objectives

- The overall objective of the proposed project is to further optimize our $Pd_{60}Cu_{40}$ (weight %) alloy membranes on porous supports for $H_2$ separation with respect to minimizing the membrane thickness while maximizing hydrogen flux and selectivity
- Other basic science objectives include an investigation of:
  - » Influence of alloy composition
  - » Effect of impurities such as carbon
  - » Effect of surface structure, particularly those resulting from oxidation and rereduction
  - » Flux reduction or inhibition due to gases such as CO, $CO_2$, $H_2O$, and $H_2S$

# What is a Membrane?

- A membrane is a barrier between two phases
- It can be used to separate a mixture (A & B) if one component (A) permeates through the membrane faster than the others
- *Example*: A balloon filled with He shrinks faster than a balloon filled with air
- Basis for gas separations using polymer membranes

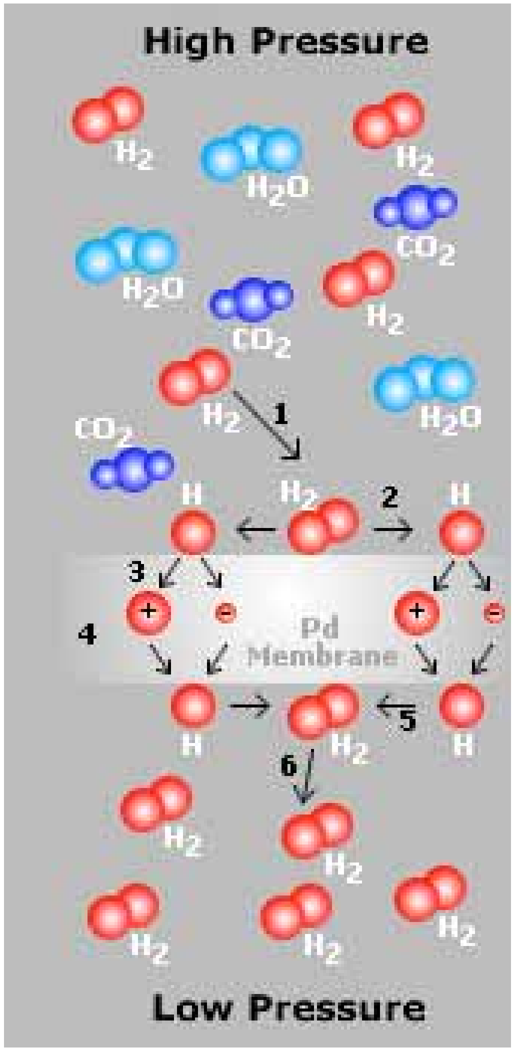


# Membrane Performance Parameters

- Permeance = pressure-normalized flux
  - Permeance = flux divided by driving force
  - Moles/m$^2$ •s•Pa or cm$^3$(STP)/cm$^2$•s•cm Hg,10$^{-6}$ cm$^3$(STP)/cm$^2$•s•cm Hg = 1 gas permeation unit or GPU, ft$^3$(STP)/ft$^2$•hr•psia or SCFH/ft$^2$•psia
  - Property of the particular ***membrane***
- Permeability = flux/$\nabla p \ (pressure \ \ gradient)$
  - Permeability = P = flux normalized by driving force and thickness
  - Moles•m/m$^2$ •s•Pa or cm$^3$(STP)•cm/cm$^2$•s•cm Hg
  - 10$^{-10}$ cm$^3$(STP)•cm/cm$^2$•s•cm Hg is 1 Barrer
  - Property of the ***material***
- $\alpha_{ij}$ = separation factor (dimensionless)
  - $(conc_i / conc_j)_{perm} / (conc_i / conc_j)_{feed}$ for liquids
  - Ratio of permeances or permeabilities for gases & vapors
  - Analogous to relative volatility in distillation
- Driving force for hydrogen permeation different!

# Why Pd Membranes?

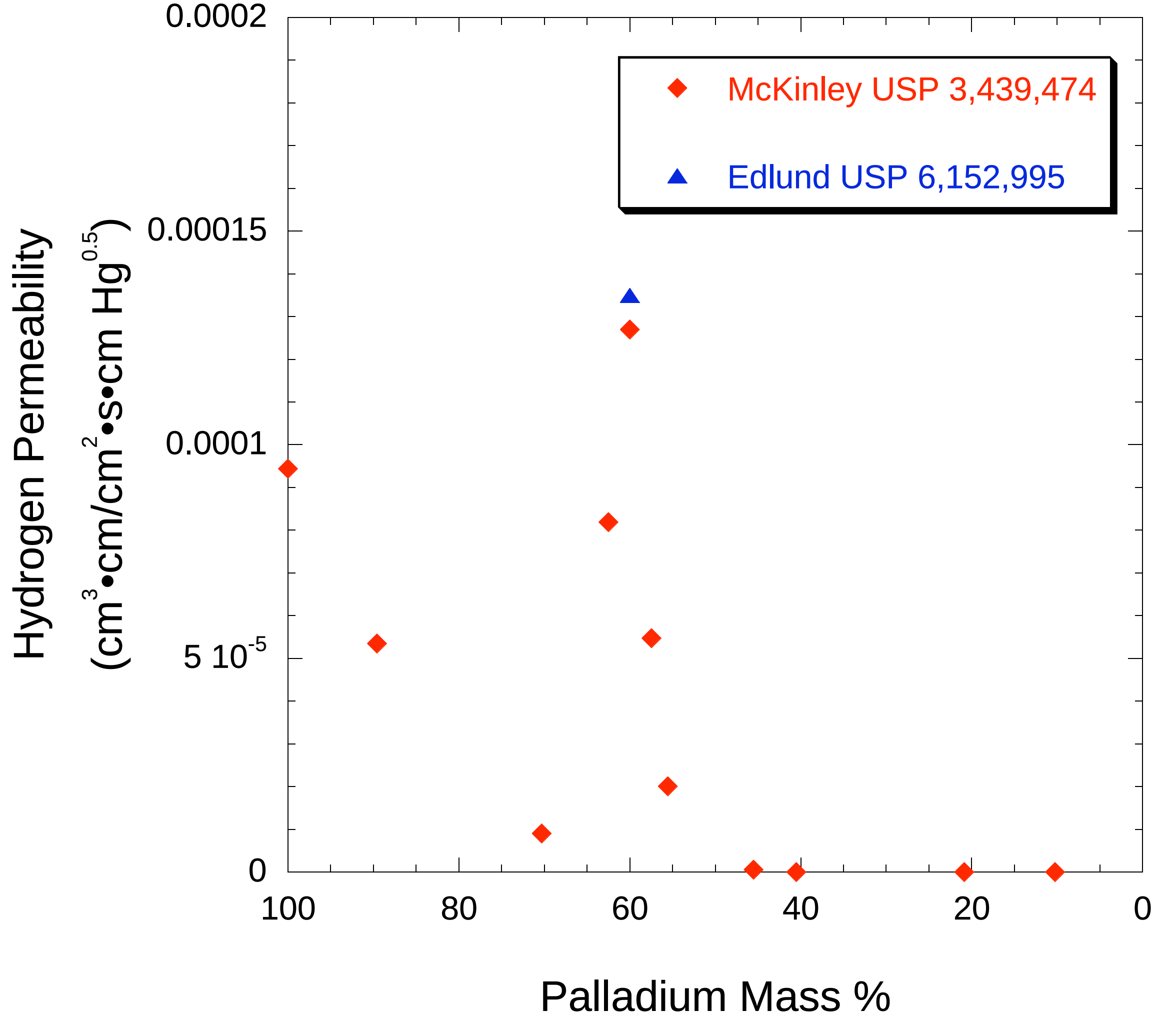
- Rate processes in series
  - Adsorption of $H_2$ molecules (1)
  - Dissociation of $H_2$ into atomic H (2)
  - Atomic H dissolves into the Pd membrane (3)
  - Atomic H diffuses across the membrane (4)
  - Recombination of atomic H into $H_2$ (5)
  - Desorption of the $H_2$ molecules (6)
- Pd and its alloys are excellent catalysts for dissociation of $H_2$ (step 2)
- Flux equation when diffusion (3) is limiting
  - $$J_H = \frac{P_H}{\ell_m}\left(\sqrt{p_{H_2,\,feed}} - \sqrt{p_{H_2,\,permeate}}\right)$$
- Permeability a function of solubility and diffusion rate of **atomic** hydrogen
- Potential for perfect selectivity



# Why Palladium Alloy Membranes?

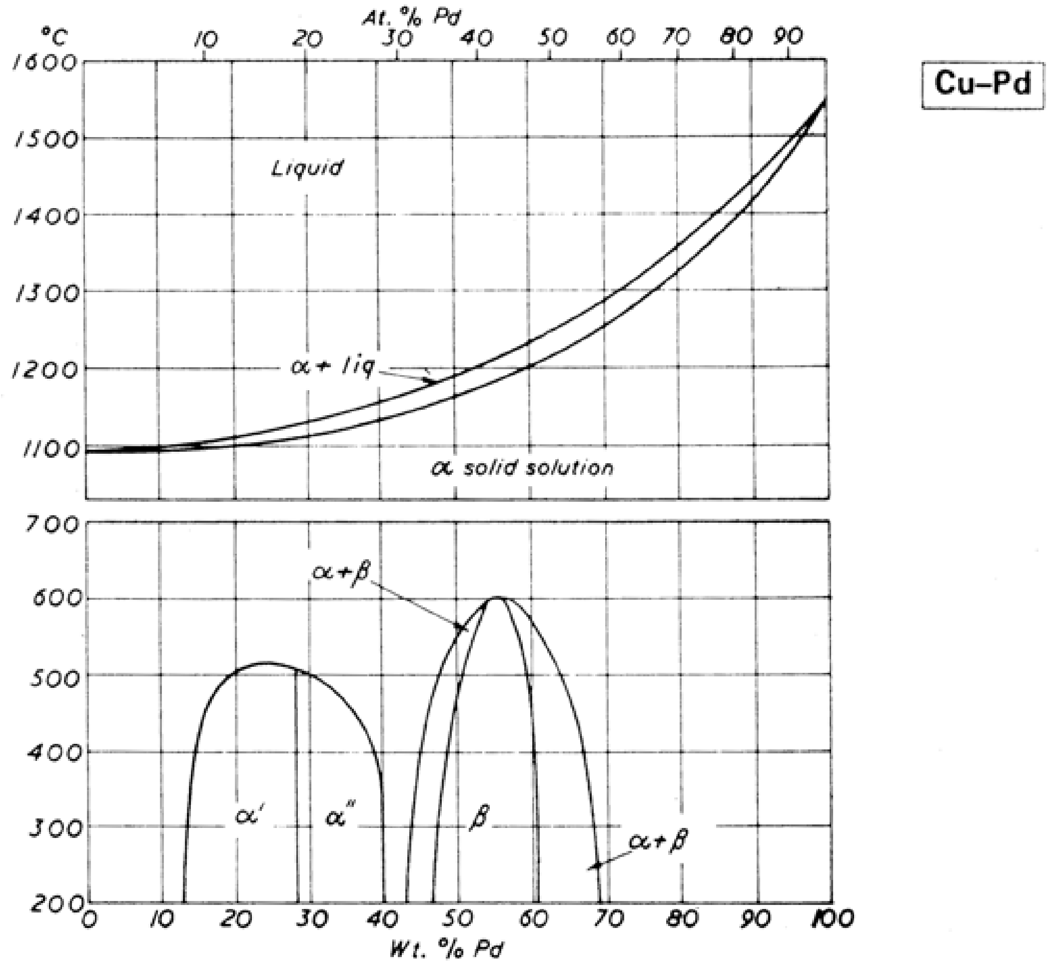
- Alloys have higher permeability
  - » e.g. 27% Ag, 6% Ru, 40% Cu, 5% Au
- Avoid $\alpha \rightarrow \beta$ phase transition in pure Pd
  - » Eliminates warping, cracking
- $Pd_{60}Cu_{40}$ mass %
  - » Cheaper
  - » Resistant to $H_2S$
  - » Robustness w.r.t. thermal cycling
  - » Excellent dimensional stability (small degree of swelling)

# Influence of Pd-Cu Alloy Composition @ 350 °C

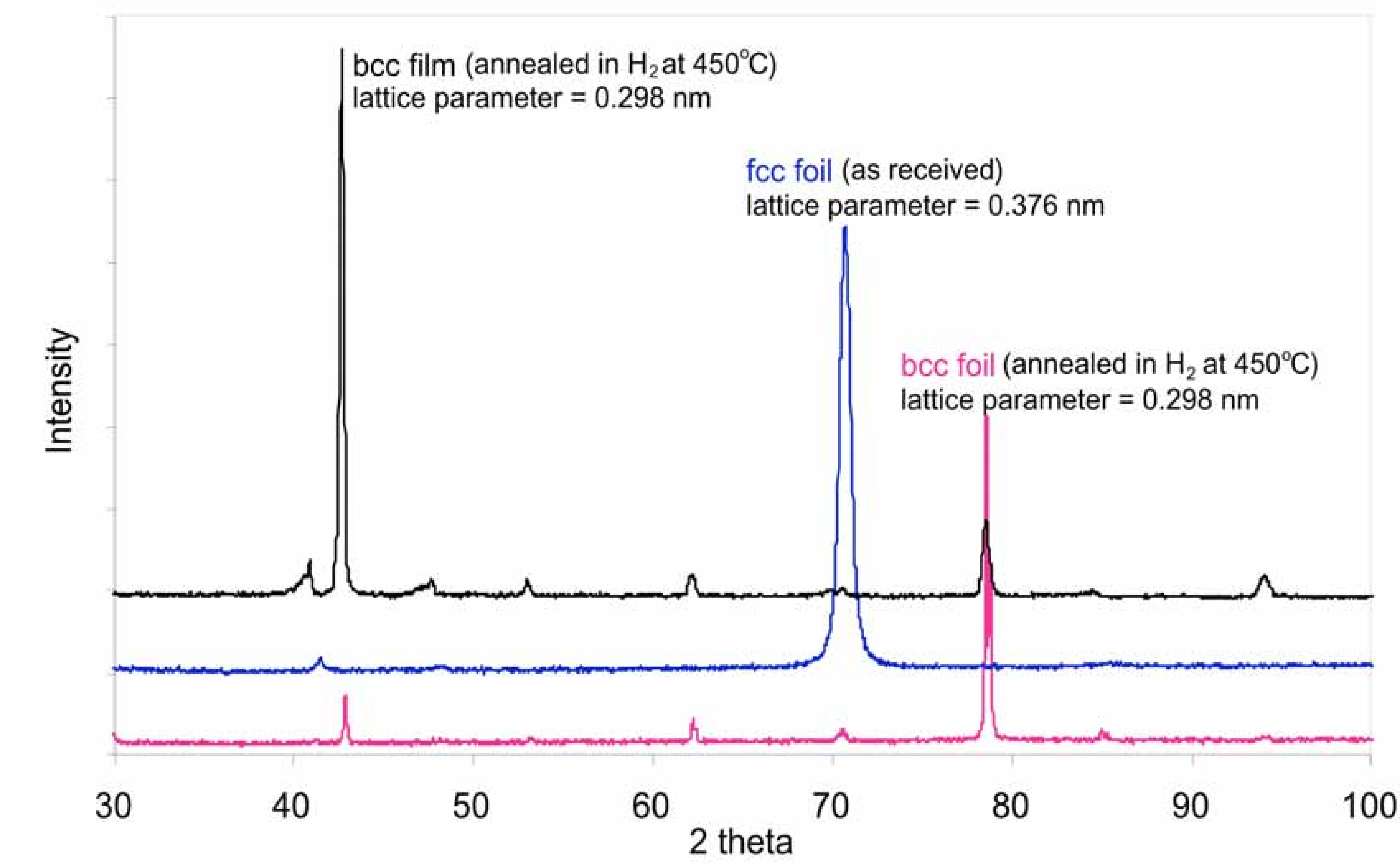


# Pd-Cu Phase Diagram

- Phase diagram from Smithells, Colin J., *Smithells Metals Reference book*, Eric A. Brandes, Editor,Butterworth-Heinemann; 6th Ed, December 1983, London.
- α phase is fcc
- β phase is CsCl (bcc)



# XRD of $Pd_{60}Cu_{40}$ Film and Foil



# Pd and Pd-Cu Alloy *Composite* Membranes

- Synthetic strategy to make a **thin**, composite Pd membrane on an porous ceramic or metal support
  - » Idea from work of Uemiya and Kikuchi, *Chem. Lett.*, 1687, 1988
  - » Our group has made Pd, Pd-Au, Pd-Cu membranes using a variety of substrates since 1990
  - » Pd or Pd alloy film on the inside OR outside of porous ceramic and outside of stainless steel filters
  - » Filter substrates can be symmetric (constant pore size) or asymmetric (gradient in pore size)
    - – Substrates purchased from or donated by Pall Corp, Mott, CoorsTek
    - – Pore sizes 0.02 µm - 0.5 µm


# Why Electroless Plating?

- Advantages
  - » Scale-up feasible
  - » Simple, easy to control
  - » Can plate complex geometries
  - » Consecutive plating followed by annealing to produce alloys
  - » Produces high flux membranes
- Disadvantages
  - » Slow kinetics compared to PVD (sputtering)
  - » Possible contamination from carbon
  - » Pd membrane thickness related to support surface roughness

# Fabrication of Pd–Alloy Composite Membranes

- Deposit Pd seeds or crystallites on cut (7 cm) support tube
- Sequentially deposit Pd and then Cu under osmotic pressure gradient using electroless plating
  - » Deposit Pd first, perform $N_2$ leak test
  - » Osmotic pressure plating due to Yeung and Varma, *AIChE J.*, 1995. **41**(9): p. 2131.
  - » Roa, et al., *Desalination*, **147**, 411-416(2002).
- Anneal at high temperature (350-550 °C depending on thickness) under hydrogen
  - » Intermetallic diffusion of Pd and Cu layers produces homogeneous alloy film
- Conduct permeability tests
- Destructive analysis of film: XRD, AFM, SEM & EDAX

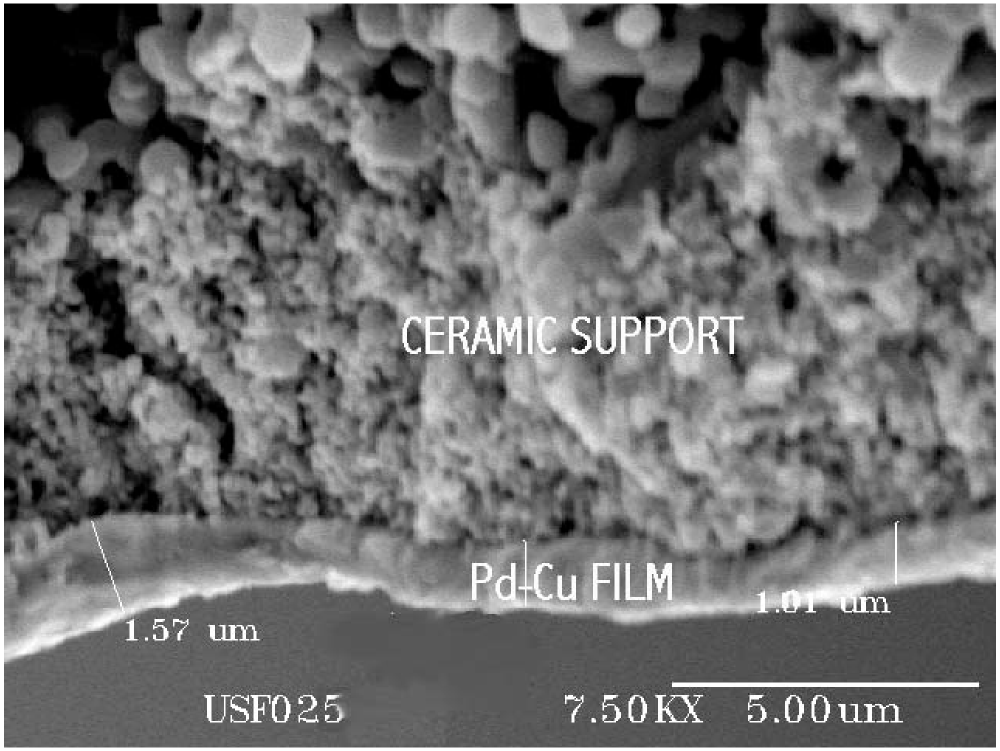
# Hydrogen Separation – Technical Targets

| Performance Criteria | 2007 Target | 2010 Target | 2015 Target |
|---|---|---|---|
| Flux SCFH/$ft^2$ @100 psi $\Delta$P $H_2$ partial pressure & 50 psia permeate side pressure | 100 | 200 | 300 |
| Operating Temp, $^oC$ | 400-700 | 300-600 | 250-500 |
| S tolerance | Yes | Yes | Yes |
| Cost, $/$ft^2$ | 150 | 100 | <100 |
| WGS Activity | Yes | Yes | Yes |
| $\Delta$P Operating Capability, system pressure, psi | 100 | Up to 400 | Up to 800 to 1000 |
| CO tolerance | Yes | Yes | Yes |
| Hydrogen Purity | 95% | 99.5% | 99.99% |
| Stability/Durability (years) | 3 | 7 | >10 |

From Office of Fossil Energy *Hydrogen from Coal RD&D Plan*, June 10, 2004 - DRAFT

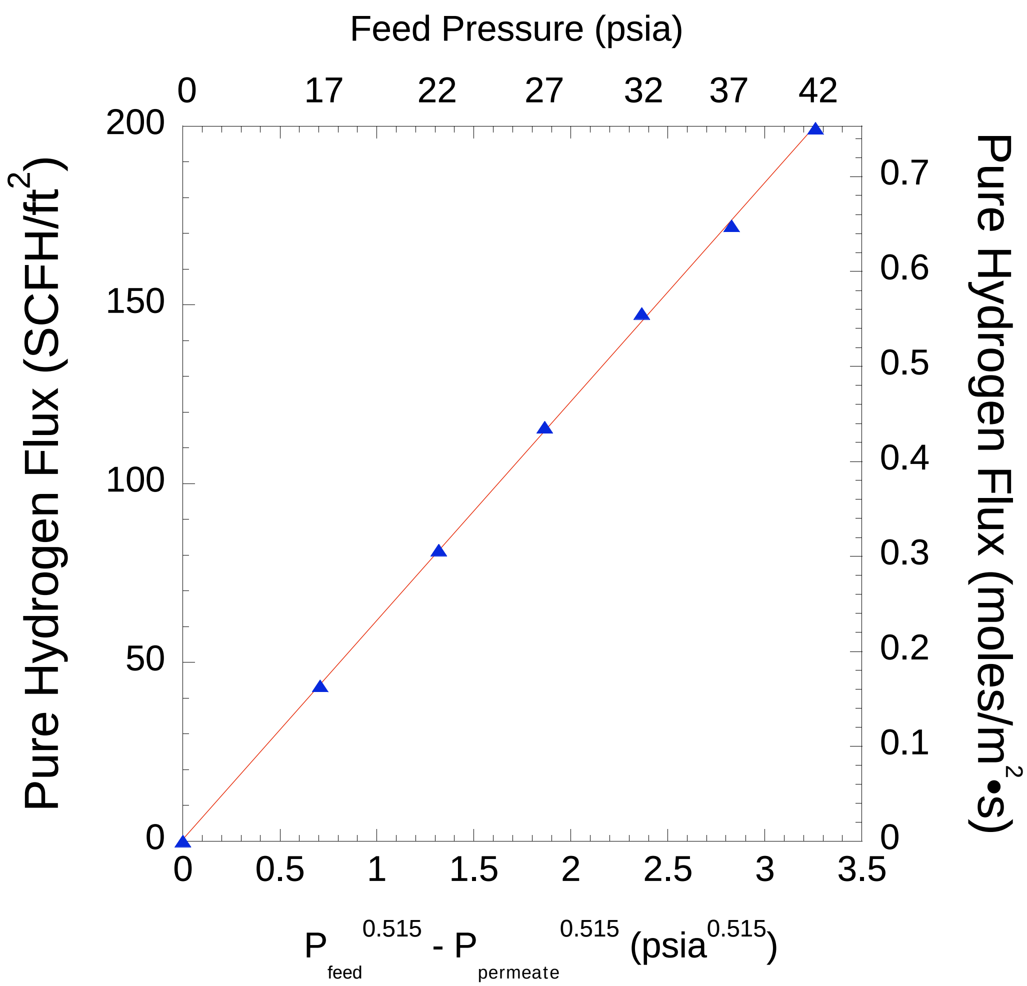
# Pd-Cu Composite Membrane #25b

- Pd-Cu alloy #25b
  - » 60 weight % Pd, 40% Cu alloy film produced
  - » "Apparent" or **visible** thickness of ~ 1.5 µm by SEM
  - » Total thickness unknown, but probably ~ 2.5 µm due to penetration into support
  - » Exekia (Pall) 50 nm ceramic filter support
  - » SEM scale bar is 5 µm
- Roa, F. and J. D. Way, *Ind. Eng. Chem. Res.*, **42**, 5827-5835(2003).



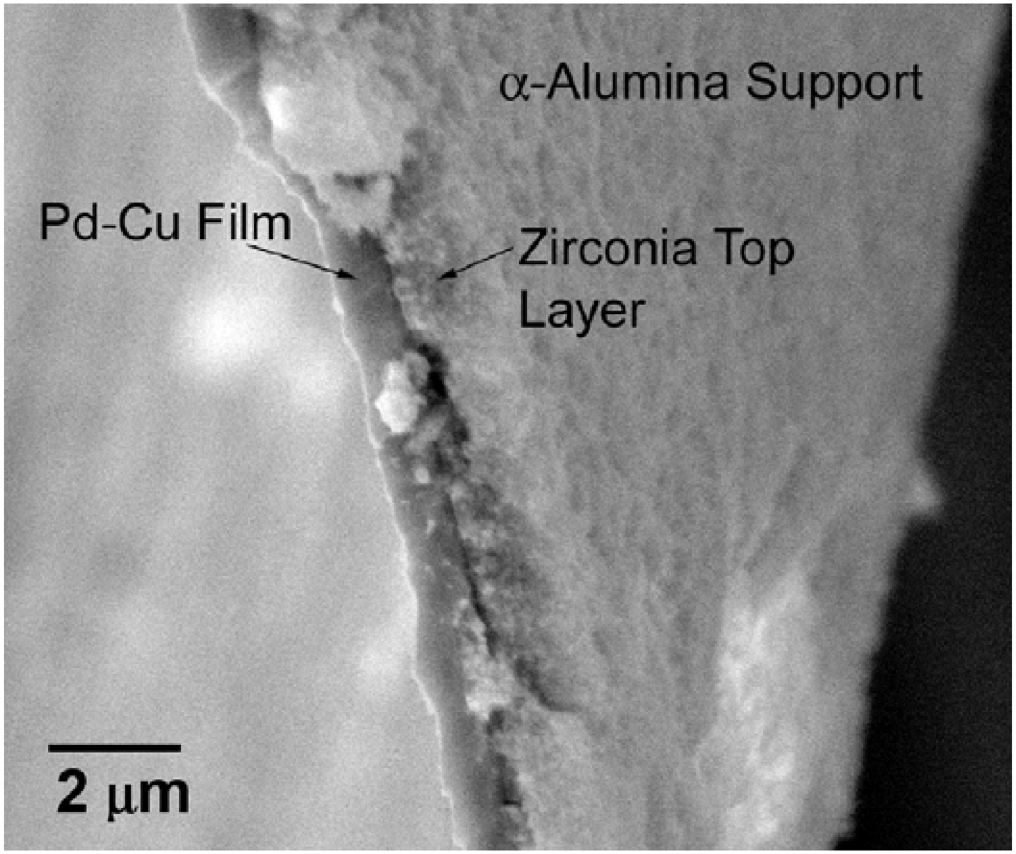
# Pure $H_2$ Flux Data for Membrane #25b at 350 °C

- 8 cm long, #25b
- "n" value in Sievert's law by regression
  - » $J = \frac{P}{l}\left(p_f^n - p_p^n\right)$
- n =0.515 compared to 0.5 from theory
- *Very high* flux!
  - » 2x the permeance of IdaTech 25 µm Pd-Cu foil (USP 6,152,995)
- $H_2$ permeance = 61.4 SCFH/ft$^2$/psia$^{0.515}$
- $H_2$ flux at DOE conditions = 350 SCFH/ft$^2$



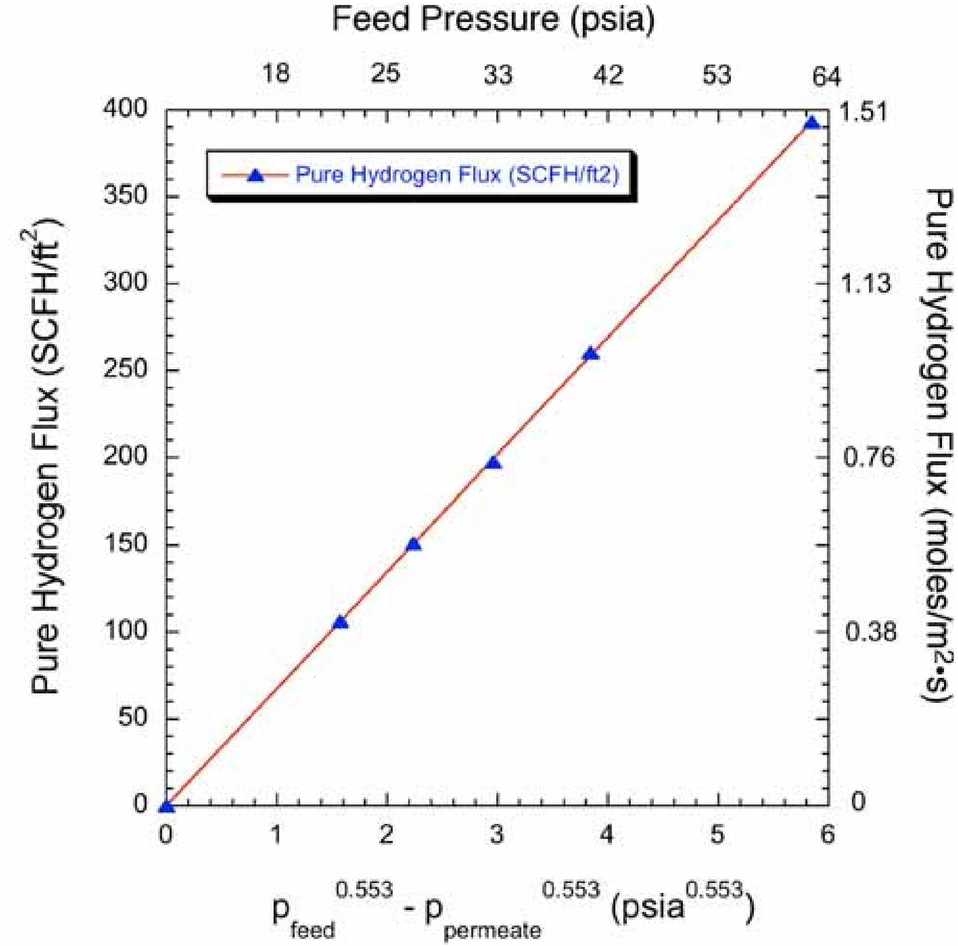
# Pall #4 Cross Section Image

- Apparent Pd-Cu film thickness ~1.3 µm
- Similar thickness to #25b
- Film composition from EDAX 95 mass % Pd, 5 % Cu
- Reformulated Pd plating solution to reduce carbon impurities
- Support 20 nm Exekia (Pall) $ZrO_2$/alumina tubular ceramic ultrafilter



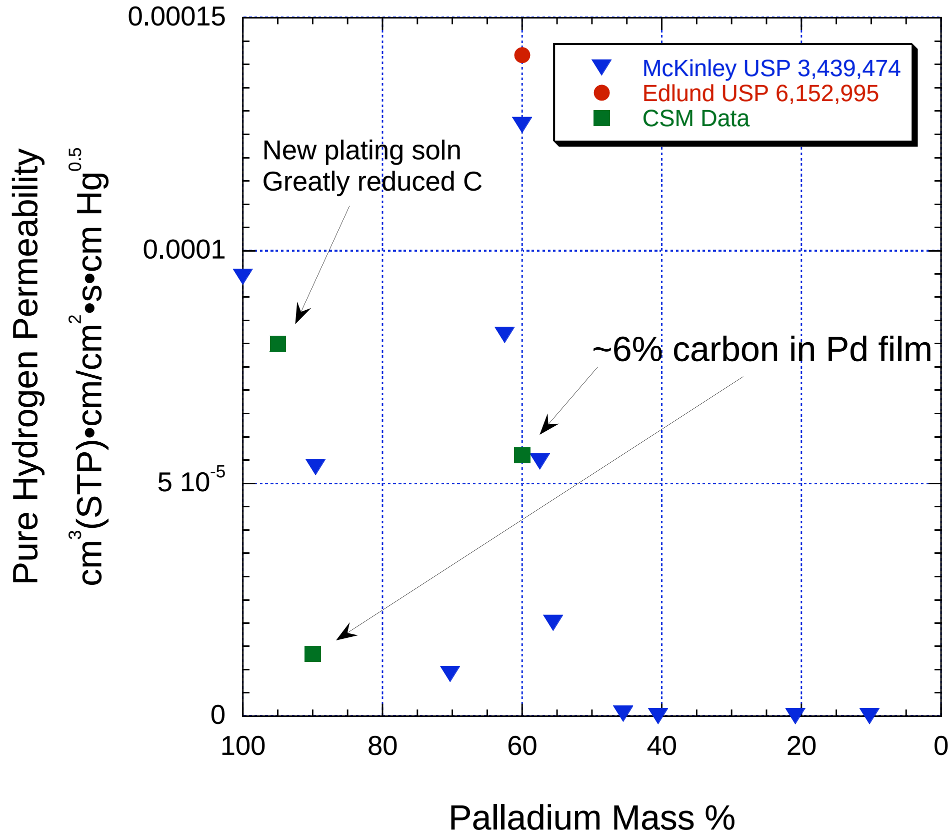
# Pure $H_2$ Flux for Pd-Cu Composite Membrane at 365 °C

- $H_2$ flux at DOE target conditions (150 psia feed, 50 psia permeate)
  - » 488 SCFH/ft$^2$ = 248 cm$^3$/cm$^2$/min
- Exponent in flux equation is 0.553, close to theoretical value of 0.5
- Ideal $H_2/N_2$ separation factor is 96 for a 50 psig feed pressure
- $H_2$ permeance = 67.2 SCFH/ft$^2$/psia$^{0.553}$



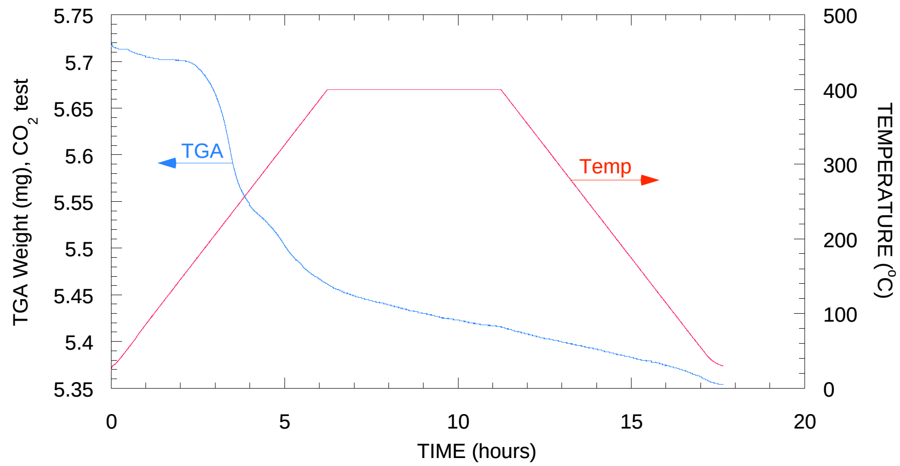
# $H_2$ Permeance Comparison

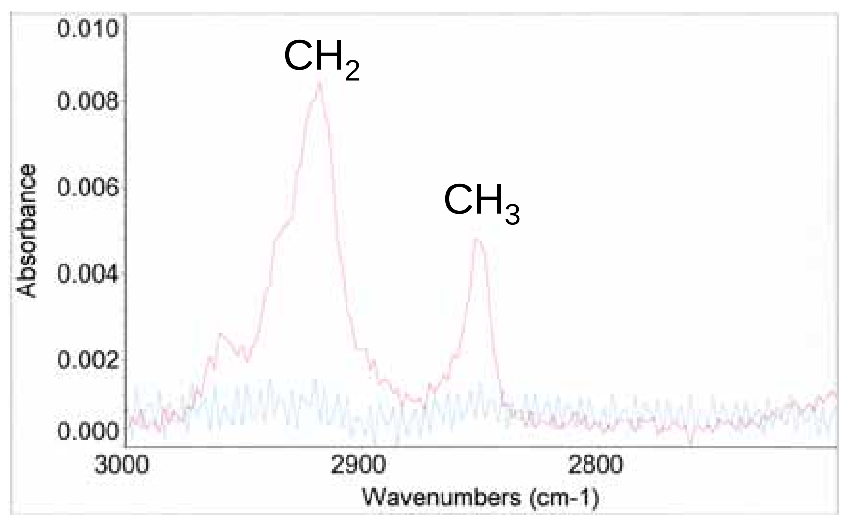
- $Pd_{95}Cu_5$ alloy has only 62.5% of the $H_2$ permeability of the $Pd_{60}Cu_{40}$ alloy
- Why doesn't that hold for our composite membranes?
  - » Thicknesses the same, but the permeance of the 95% Pd alloy membrane about 10% higher!
  - » Assume total thickness 2.5 µm
- Our "old" plating solution creates significant carbon contamination in the Pd film!
  - » Source of contamination is the EDTA stabilizing agent
  - » Carbon reduces $H_2$ permeability!
  - » Error in Pd % also possible



# Evidence of Carbon Contamination

- Top figure TGA of Pd film in $CO_2$ atmosphere, $CO_2$ reacts with C, membrane is catalyst
  - » Mass loss corresponds to 6.4%
  - » No mass change in argon
- Bottom figure FTIR spectrum of Pd on Si, can see $CH_2$ and $CH_3$ peaks
- Total carbon analyzer measured 7% carbon
- $CO_2$ exposure to thin membranes with carbon can result in film rearrangement and pore formation
- Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, *Ind. Eng. Chem. Res.*, **43**(15), 4188-4198(2004).

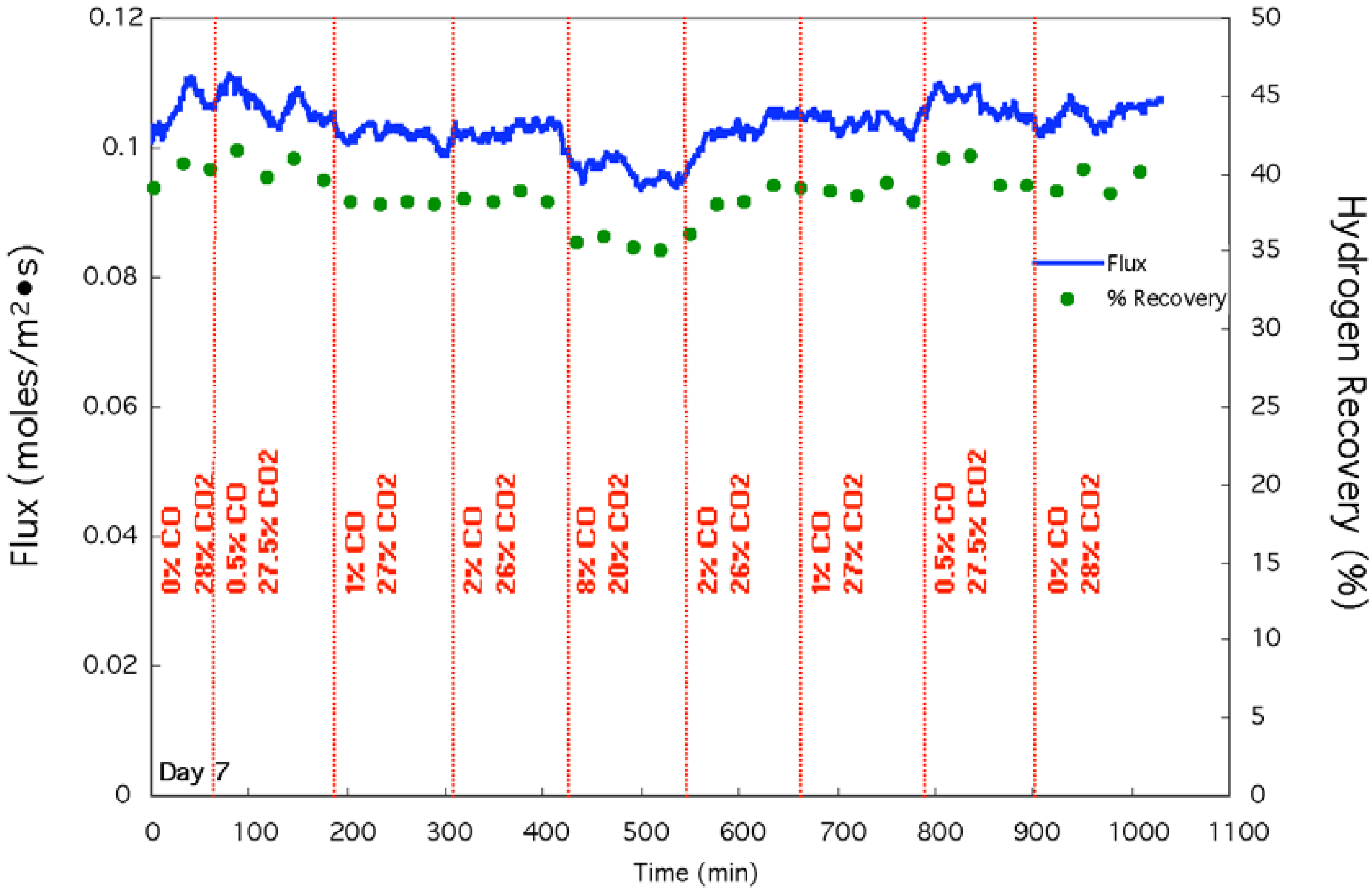


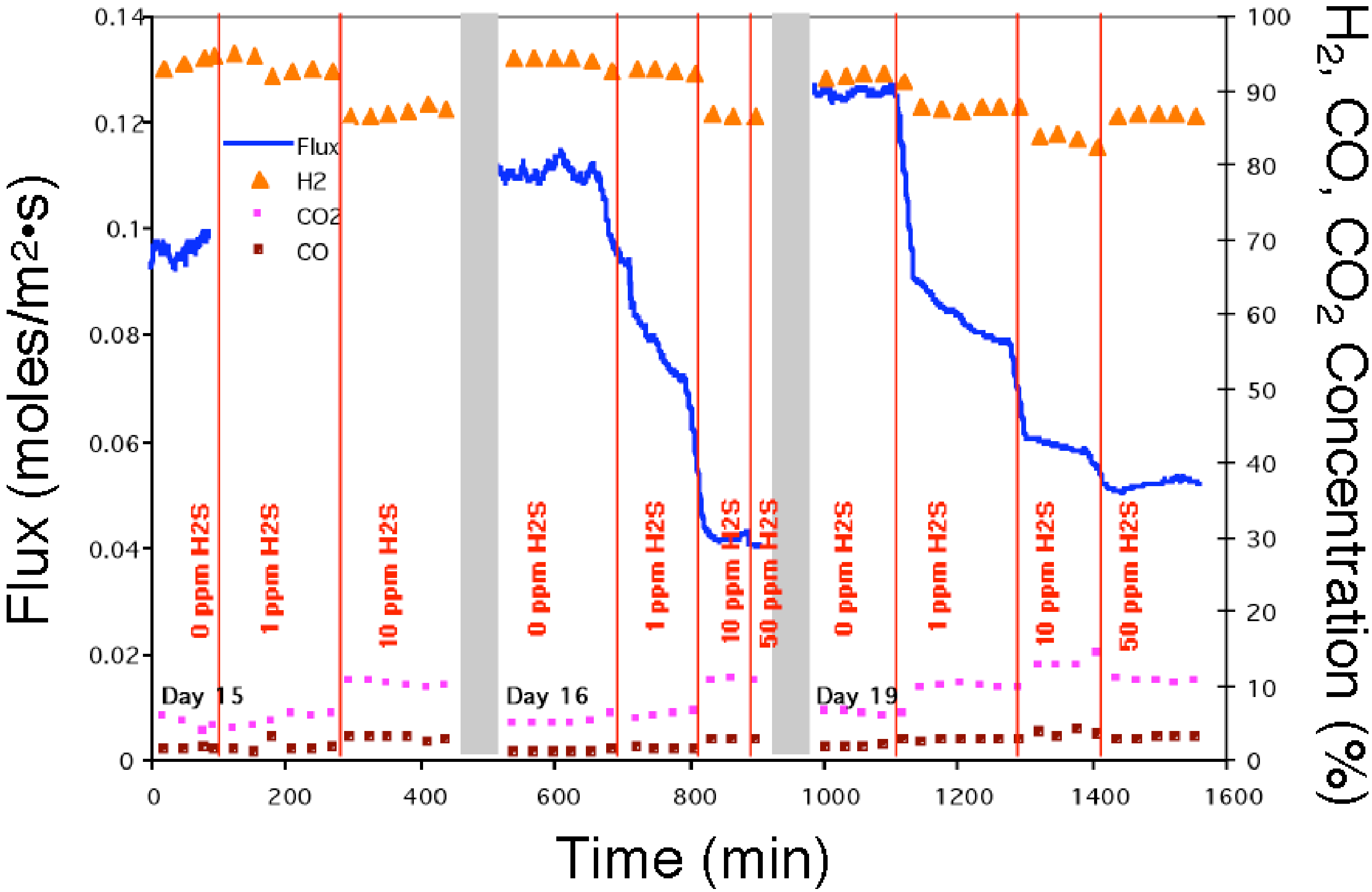
# Gas Mixture Experiments

- Objective to investigate the separation of $H_2$ from a complex gas mixture simulating the product stream from the water-gas shift reaction
  - » Industrial collaborator specified conditions
  - » Mixture experiments performed at TDA Research, Inc.
  - » Membranes made from OLD plating solution, assume carbon impurities present
- Temperature:  350 - 450 °C
- Feed pressure up to 15 bar gauge = 225 psig
  - » 0.2 µm pore size symmetric $Al_2O_3$ support used, 7 µm PdCu film
  - » Graphite ferrule seals in stainless steel compression fittings
- Feed gas: 51% $H_2$, 26% $CO_2$, 21% $H_2O$, 2% CO, 1 ppm $H_2S$
- Investigate the effects of $CO/CO_2$ concentration, $H_2S$ concentration, and use of a sweep gas

# Effect of CO & $CO_2$ on $H_2$ Flux from WGS Mix @ 350 °C, $P_{feed}$= 250 psig, No $H_2S$



# Effect of $H_2S$ Concentration in WGS Mixture @ 350 °C, 250 psig Pressure



# Effect of $H_2S$ Concentration in WGS Mixture @ 350 °C, 250 psig Pressure

- See ~50% inhibition, or reduction of $H_2$ flux due to $H_2S$ concentration of 50 ppm when steam is present
- Membrane exposure to pure $H_2$ after $H_2S$ (grey bars)
- $H_2$ flux recovers after three exposures to 10 ppm ($3 \cdot 10^{-3}$ psia partial pressure) and two runs with 50 ppm (0.013 psia) $H_2S$
- Membrane **failed** when exposed to 250 ppm = 0.065 psia partial pressure, approximately at $H_2S$ concentration when inhibition reaches 100%
- Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, “Pd and Pd-Cu Membranes: Inhibition of $H_2$ Permeation by $H_2S$,” *Journal of Membrane Science*, **254**, 49-62(2005).

# Cost of Pd in a Composite Membrane

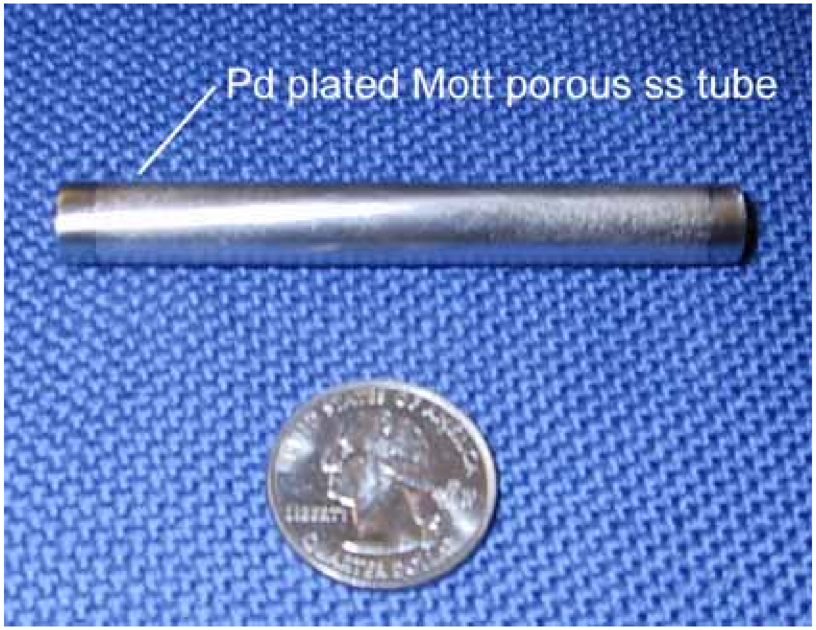
- Common misconception: “The cost of Pd is too large for a system to be practical”
- For a 25 cm long, 2 micron thick $Pd_{60}Cu_{40}$ film on an asymmetric (graded porosity) ceramic filter support, the Pd costs \$0.71 and the support costs \$240
  - » Pd spot price 6-2-05 = \$185/troy ounce = \$5.95/g
    - – 1 troy ounce = 31.1 g
  - » My retail cost for Pd from $PdCl_2$ is \$15.00/g
  - » *Pd would be <0.5% of the membrane materials cost!!*
- \$12.00 (retail) < Pd cost/ft$^2$ < \$5.00 (from Pd spot price)

# Comparison with $H_2$ Flux Targets

| Performance Criteria | 2007 Target | 2010 Target | 2015 Target | CSM Pd-Cu |
|---|---|---|---|---|
| Flux SCFH/ft$^2$ @100 psi ΔP $H_2$ partial pressure & 50 psia permeate side pressure | 100 | 200 | 300 | 488 |
| $H_2$ Permeance or Flux/driving force, SCFH/ft$^2$/psia$^{0.5}$ | 19.3 | 38.6 | 57.9 | 67.2 |
| Operating Temp, °C | 400-700 | 300-600 | 250-500 | RT – 600 |
| S tolerance | Yes | Yes | Yes | Yes, OK for [$H_2S$] ≤ 250 ppm with steam |
| Cost, \$/ft$^2$ | 150 | 100 | <100 | Depends on Support |
| WGS Activity | Yes | Yes | Yes | Yes |
| ≤P Operating Capability, system pressure, psi | 100 | Up to 400 | Up to 800 to 1000 | Tested to 400 psig feed |
| CO tolerance | Yes | Yes | Yes | Yes |
| Hydrogen Purity | 95% | 99.5% | 99.99% | Need to do mixed gas tests |
| Stability/Durability (years) | 3 | 7 | >10 | ? |

# Planned Future Research

- Optimize membrane Pd-Cu alloy composition with new plating solution
  - » Higher fluxes should be possible
- Gas mixture experiments with Pd-Cu membranes with reduced carbon content
- High T permeation tests with Pd/porous stainless steel membranes
  - » Pd-Cu alloys
  - » Effectiveness of diffusion barrier
- More analysis to quantify amount and distribution of carbon impurities
  - » X-ray scattering, XPS/Auger



# Conclusions

- Pd/Cu alloy composite membranes can be made by sequential electroless plating and annealing
- Thickness reduced by decreasing surface roughness of support and using asymmetric support structure
  - » ~2.5 µm thick, 95% Pd, 5% Cu, pure $H_2$ flux ~ 1.5 mol/$m^2$•s at 50 psig, 365 °C
  - » Exceeded DOE Fossil Energy pure $H_2$ flux target
  - » Flux calculated at DOE target conditions = 488 SCFH/$ft^2$
  - » Materials cost controlled by cost of ceramic support

# Conclusions

- Pd-Cu composite membrane tested for three weeks with simulated equilibrium water-gas shift gas mixture feed at 350 °C and 250 psig feed pressure
  - » Mixture contained $H_2$, $CO_2$, CO, $H_2O$, and $H_2S$
  - » In WGS mixture without $H_2S$, CO inhibits (reduces) $H_2$ flux, but does not poison membrane
  - » 2-8 mole % CO in feed gas reduced $H_2$ flux by ≤ 17% @ 350 °C
  - » Exposure to CO and $CO_2$ did not cause membrane fouling or damage
  - » Low $H_2S$ concentrations, ≤ 50 ppm, also show inhibition effect where $H_2$ flux recovers if $H_2S$ concentration reduced
  - » High $H_2S$ concentrations, ≥ 250 ppm, cause pore formation and membrane failure

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  - » Golden Technologies/CoorsTek, Pall Corporation
- Former/Current Grad Students:
  - » Omar Ishteiwy, MS candidate
  - » Dr. Ames Kulprathipanja, PhD 2003, Mesoscopic Devices, LLC
  - » Michael Block, MS 2003, Johns Manville, Inc.
  - » Dr. Fernando Roa, PhD 2003, Intel Corporation
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  - » Dr. John Collins, PhD 1993, BP Research